

## REACTION OF DISILANES WITH ACETYLENES

### I. STEREOSELECTIVE ADDITION OF METHOXYMETHYLDISILANES TO PHENYLACETYLENE CATALYZED BY GROUP-VIII METAL PHOSPHINE COMPLEXES

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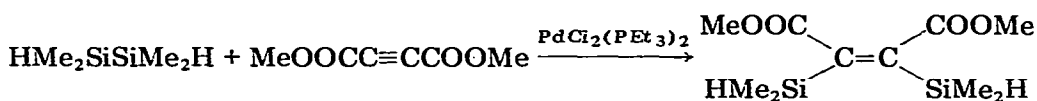
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#### Summary

Addition reactions of methoxymethylidisilanes to phenylacetylene in the presence of various triphenylphosphine complexes of Ni, Rh, Pd and Pt were investigated. Palladium and platinum complexes,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{Pt}(\text{PPh}_3)_4$  were found to be effective catalysts for the double silylation, giving adducts, *cis*- $\alpha,\beta$ -disilylated styrene derivatives selectively. It also was shown that hexamethyldisilane reacted with the acetylene. A possible mechanism for the stereoselective and regioselective double silylation is proposed. The *cis*-adducts isomerized to the corresponding *trans* isomers in the presence of disilane and a palladium complex catalyst.

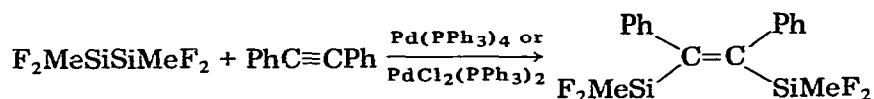
#### Introduction

The double silylation of acetylenic compounds with disilanes was first reported by Kumada et al. who found that the reaction of *sym*-dihydrotetramethyldisilane with dimethyl acetylenedicarboxylate, catalysed by phosphine-palladium(II) complexes, gave dimethyl  $\alpha,\alpha'$ -bis(dimethylsilyl)maleate [1].

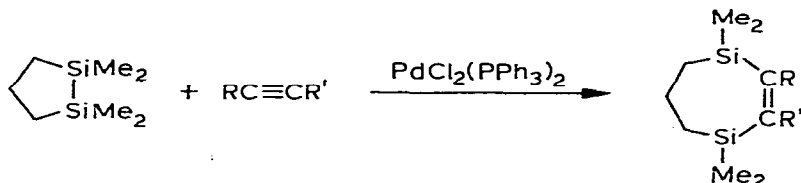


They have also reported that highly reactive fluorinated disilanes add to acetylenes in the presence of palladium complex catalysts to give double silylation

products in 60–95% yields, but hexamethyldisilane did not react [2], e.g.:



Sakurai and coworkers independently reported that double silylation occurs in the reaction between a strained disilacycloalkane and an acetylene in the presence of a palladium(II) catalyst to give a 1,4-disilacycloalk-2-ene in good yield [3], e.g.:



They noted that hexamethyldisilane, an example of the unstrained hexaorgano-disilane, also undergoes this reaction but only a low yield of the disilylated product was obtained.

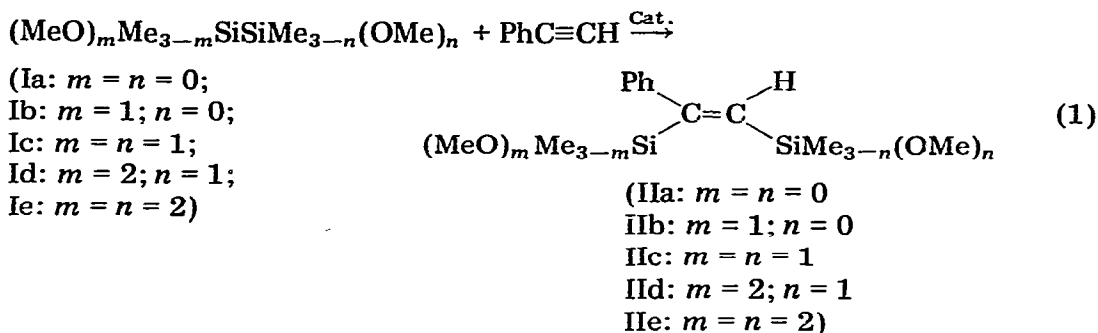
These precedents might cause one to believe that the double silylation is observable only with disilanes of special structures such as hydro-, fluoro- and strained-disilanes. However, a thermochemical consideration on the reaction between a disilane and an acetylene to give the corresponding disilylethylene leads to a calculated value of ca. -40 kcal/mol for the heat of reaction [4–6]. This means that the double silylation should be quite exothermic and should occur with a wide variety of disilanes under appropriate reaction conditions. The present paper describes the reaction of various methoxymethyldisilanes, as well as hexamethyldisilane, with phenylacetylene catalysed by Group VIII—metal triphenylphosphine complexes. Methoxydisilanes are chosen as substrates in view of our continuing interest in their reactions [7–10]. The stereochemistry of the reaction and geometrical isomerism of the adducts were investigated.

## Results and discussion

### *Reactions of phenylacetylene with methoxymethyldisilanes in the presence of various Group VIII-metal phosphine complex catalysts*

In order to find effective catalysts for the reaction shown in eq. 1, the catalytic activities of six phosphine complexes, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, RhCl(PPh<sub>3</sub>)<sub>3</sub>, RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pt(PPh<sub>3</sub>)<sub>4</sub>, were examined, employing the reactions of *sym*-dimethoxytetramethyldisilane and dimethyltetramethoxydisilane as standards. The results for the double silylation catalysed by these complexes are summarized in Table 1.

It is seen from Table 1 that, for the reaction of *sym*-dimethoxydisilane, three complexes, Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pt(PPh<sub>3</sub>)<sub>4</sub>, were catalytically active to give the double silylation product in fair to good yields (34–80%). However, the yields of the products were lower in the reactions catalysed by the latter two complexes than those catalysed by the former and the *cis* to *trans* isomer ratio also was somewhat lower. For the reaction with *sym*-dimethyltetrameth-



oxydisilane, the palladium(0) complex catalyst also was effective, giving 56–70% yields of product. From these results it is evident that the palladium(0) complex is the best catalyst among those examined for the double silylation of this type with methoxymethyldisilane.

The double silylation of phenylacetylene in the presence of a palladium(0) complex catalyst using hexamethyl-, methoxypentamethyl- and 1,1,2-trimethoxy-1,2,2-trimethyldisilane was next investigated. The reactions of these disilanes according to eq. 1 proceeded smoothly to give the corresponding products in good yields (56–80%), except for hexamethyldisilane (18–26%). The results using these disilanes as well as di- and tetra-methoxydisilanes are listed in Table 2. There is no remarkable difference in yields between the methoxydisilanes. On the other hand, for the reactions of hexamethyl- and monomethoxymethyl-disilane, higher yields were obtained in a closed system than in an open system.

The most important feature, however, was that the double silylation of phenylacetylene occurred as expected with all the disilanes as predicted from

TABLE 1

DOUBLE SILYLATION OF PHENYLACETYLENE WITH METHOXYDISILANES IN THE PRESENCE OF VARIOUS PHOSPHINE COMPLEXES AS CATALYST<sup>a</sup>

Disilane	Catalyst <sup>b</sup>	Temp. (°C)	Timeq (h)	Adduct		
				Yield (%) <sup>c</sup>	Ratio <i>cis/trans</i>	
(MeO)Me <sub>2</sub> SiSiMe <sub>2</sub> (OMe) (Ic)	Pd(PPh <sub>3</sub> ) <sub>4</sub>	110	1.5	IIc	78	92/8
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	110 <sup>d</sup>	20	IIc	76	91/9
	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	140	3	IIc	45	88/12
	Pt(PPh <sub>3</sub> ) <sub>4</sub>	130 <sup>d</sup>	48	IIc	34	65/35
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	150 <sup>d</sup>	48	IIc	0	
	RhH(CO)(PPh <sub>3</sub> ) <sub>3</sub>	110	48	IIc	0	
(MeO) <sub>2</sub> MeSiSiMe(OMe) <sub>2</sub> (Ie)	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	140	40	IIc	0	
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	110 <sup>d</sup>	1.5	IIe	56	89/11
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	110 <sup>d</sup>	20	IIe	71	96/4
	Pt(PPh <sub>3</sub> ) <sub>4</sub>	130 <sup>d</sup>	20	IIe	0	
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	150 <sup>d</sup>	20	IIe	0	

<sup>a</sup> Disilane/acetylene 10/5 (mmol); unless otherwise specified, the reaction was carried out by heating under argon in an open system. <sup>b</sup> One mol % relative to the acetylene used. <sup>c</sup> GLC yield based on the acetylene. <sup>d</sup> Heated in an evacuated and sealed Carius tube.

TABLE 2

DOUBLE SILYLATION OF PHENYLACETYLENE WITH VARIOUS METHOXYMETHYLDISILANES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM <sup>a</sup>

Disilane	Method <sup>b</sup>	Time (h)	Adduct		
			Yield	(%) <sup>c</sup>	Ratio <i>cis/trans</i>
Me <sub>3</sub> SiSiMe <sub>3</sub> (Ia)	A	1.5	IIa	18	100/0
Me <sub>3</sub> SiSiMe <sub>3</sub> (Ia)	B	20	IIa	26	100/0
Me <sub>3</sub> SiSiMe <sub>2</sub> (OMe) (Ib)	A	13	IIb	18	99/1
Me <sub>3</sub> SiSiMe <sub>2</sub> (OMe) (Ib)	B	20	IIb	60	99/1
(MeO)Me <sub>2</sub> SiSiMe <sub>2</sub> (OMe) (Ic)	A	1.5	IIc	78	92/8
(MeO)Me <sub>2</sub> SiSiMe <sub>2</sub> (OMe) (Ic)	B	20	IIc	77	91/9
(MeO) <sub>2</sub> MeSiSiMe <sub>2</sub> (OMe) (Id)	A	1.5	IIId	75	100/0
(MeO) <sub>2</sub> MeSiSiMe <sub>2</sub> (OMe) (Id)	B	20	IIId	67	93/7
(MeO) <sub>2</sub> MeSiSiMe(OMe) <sub>2</sub> (Ie)	A	1.5	IIe	56	89/11
(MeO) <sub>2</sub> MeSiSiMe(OMe) <sub>2</sub> (Ie)	B	20	IIe	71	96/4

<sup>a</sup> Disilane/acetylene 10/5 (mmol); 110°C; Catalyst, 1 mol % relative to the acetylene used. <sup>b</sup> A: Open system under argon; B: Closed system in a Carius tube (evacuated). <sup>c</sup> GLC yield based on the acetylene used.

the calculated exothermicity of the reaction. This result conflicts with the previous suggestions [2,3], because the disilanes used in our systems are by no means peculiar in structures.

#### Stereochemistry of the double silylation of the present system

The reactions of phenylacetylene with these disilanes, catalysed by the com-

TABLE 3

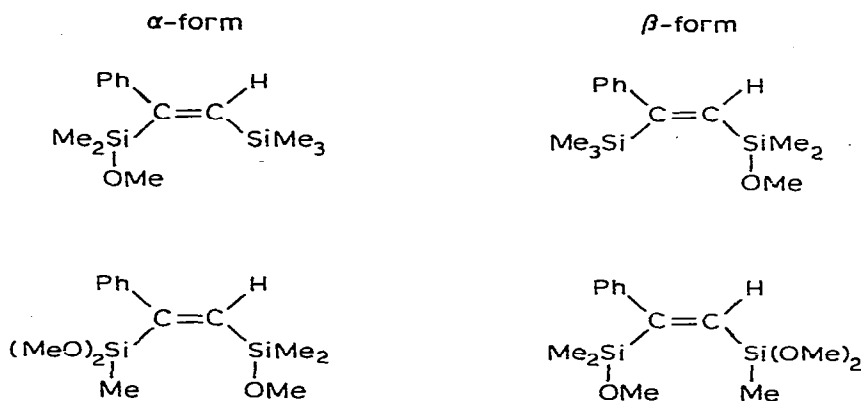
ANALYTICAL DATA AND BOILING POINTS OF THE ADDUCTS, DISILYLSTYRENES

Compound	Formula	Analysis (Found (calcd.) (%))		B.p. (°C/mmHg)
		C	H	
<i>cis</i> -IIa <sup>a</sup>	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub>	—	—	—
<i>trans</i> -IIa <sup>a</sup>	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub>	—	—	—
<i>cis</i> -IIb	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O	63.31 (63.57)	8.95 (9.15)	91/10
<i>trans</i> -IIb	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O	63.46 (63.57)	8.97 (9.15)	—
<i>cis</i> -IIc	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>2</sub>	59.92 (59.95)	8.46 (8.62)	133/10
<i>trans</i> -IIc	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>2</sub>	60.11 (59.95)	8.65 (8.62)	—
<i>cis</i> -IIId	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>3</sub>	56.33 (56.70)	8.17 (8.16)	117/10
<i>trans</i> -IIId	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>3</sub>	mol. wt. 296 <sup>b</sup>		—
<i>cis</i> -IIe	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>4</sub>	53.93 (53.81)	7.54 (7.74)	159/8
<i>trans</i> -IIe	C <sub>14</sub> H <sub>24</sub> Si <sub>2</sub> O <sub>4</sub>	53.34 (53.81)	7.45 (7.74)	—
III	C <sub>12</sub> H <sub>15</sub> Si <sub>2</sub> O	61.52 (61.48)	7.75 (7.74)	—

<sup>a</sup> Known compound (see ref. 11). <sup>b</sup> By mass spectroscopy; calcd., 296.

plex  $\text{Pd}(\text{PPh}_3)_4$ , gave *cis*-stereochemistry (Table 2). Determination of the structures of these products which could be isolated by GLC technique or by distillation were made based on  $^1\text{H}$  NMR, IR and mass spectroscopic studies and comparison with those of the literature. The results of the elemental analysis and the spectral data of the products are given in Tables 3 and 4. In the NMR spectrum for each of *trans*-IIa–IIe, the methyl substituent(s) on the silicon attached to the  $\beta$ -carbon occurred at higher field when located on the *syn*-position with respect to the benzene ring than when located on the *anti*-position. This is likely to be due to the anisotropic effect of the benzene ring, as has previously been indicated in related literature by Kumada et al. [11] and was further confirmed by the spectroscopic studies of the isomerization of the *cis*- to the *trans*-isomers (see below).

The NMR inspection of *cis*-IIb and IIc derived from the unsymmetrical disilane have shown that each of *cis* compounds was composed of two types of regioisomers,  $\alpha$ - and  $\beta$ -form, as shown below.



For example, *cis*-IIb contained the  $\alpha$  and  $\beta$ -form in a ratio of 81/19, *cis*-IIc in a ratio of 88/12.

With the generally accepted concept which has been applicable to the interpretation of a variety of homogeneous catalytic reactions, the double silylation can be interpreted tentatively in terms of a mechanism involving sequential stereoselective and regioselective processes, as shown in Scheme 1. The oxidative addition of the Si–Si bond to the palladium(0) catalyst, the formation of acetylene-coordinated complex, the insertion of the acetylene into one of the Si–Pd bonds and the reductive elimination of the product would be all reasonable processes.

With respect to the stereoselectivity in the present reaction, the  $\sigma$ -bonded palladium complex [D] in which the C–Si and C–Pd bond are placed in *syn*-position to each other would account for the *cis* stereochemistry. Analogous *cis* stereochemistry has been often quoted in the metal-catalysed hydrosilylation of acetylenes [12,13].

Direction of addition of two different silyl moieties in the double silylation with unsymmetrical disilanes, Ib and Id, is of interest. For example, the reaction of phenylacetylene with Ib gave  $\alpha$ -dimethylmethoxysilyl- $\beta$ -trimethylsilylstyrene predominantly along with the minor regioisomer. The trend of the silyl

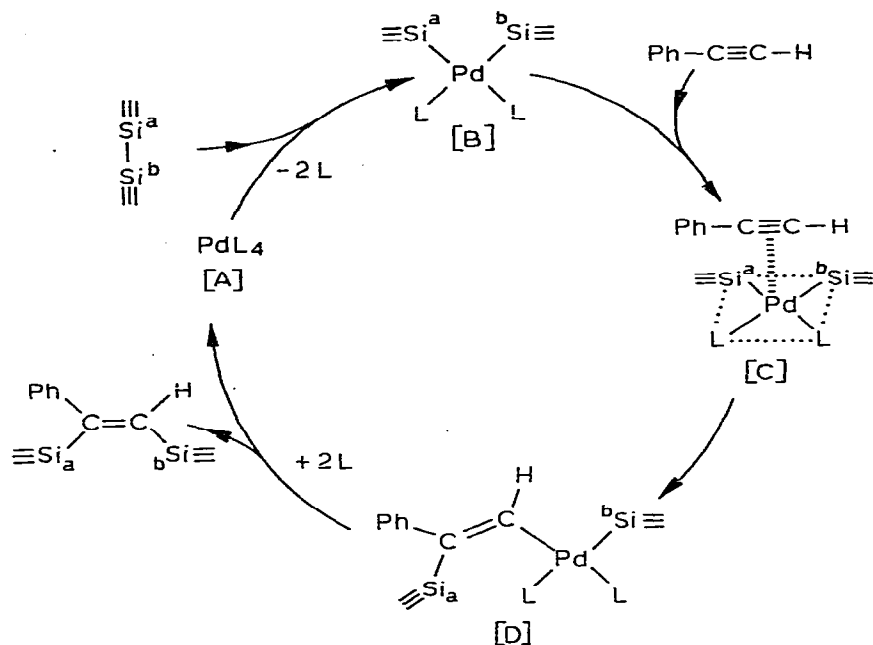
TABLE 4

NMR AND IR SPECTRA FOR THE DISILYLSTYRENE DERIVATIVES,  $\text{Ph}(\text{R}'_a)_2\text{C}=\text{CH}(\text{R}''_b)$ 

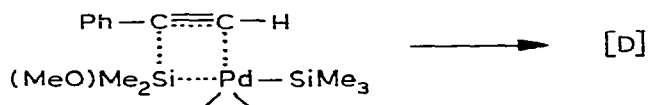
Compound	Substituent		NMR Chemical shift (CCl <sub>4</sub> ) ( $\delta$ , ppm) <sup>a</sup>					IR (neat) (cm <sup>-1</sup> )			
	R' <sub>a</sub>	R'' <sub>b</sub>	Ph	=CH	SiOMe <sub>a</sub>	SiOMe <sub>b</sub>	SiMe <sub>a</sub>	SiMe <sub>b</sub>	Si—Me	Si—O—Me	
<i>cis</i> -IIa	Me <sub>3</sub> Si	SiMe <sub>3</sub>	7.4—6.6(m)	6.36	—	—	0.20	0.14	1250	—	
<i>trans</i> -IIa	Me <sub>3</sub> Si	SiMe <sub>3</sub>	(7.05) <sup>b</sup>	(6.25) <sup>b</sup>	—	—	(0.05) <sup>b</sup>	(-0.20) <sup>b</sup>	1247 <sup>b</sup>	—	
<i>cis</i> - $\alpha$ -IIb	Me <sub>2</sub> Si	SiMe <sub>3</sub>	—	6.45	3.42	—	0.18	0.18	1257	—	
<i>cis</i> - $\beta$ -IIb	OMe	—	7.4—6.7(m)	6.20	—	3.45	0.23	0.23	1250(sh)	1091	
<i>trans</i> - $\alpha$ -IIb	Me <sub>2</sub> Si	OMe	—	6.36	3.36	—	0.11	-0.18	1250	—	
<i>trans</i> - $\beta$ -IIb	Me <sub>3</sub> Si	OMe	7.4—6.7(m)	6.28	—	3.26	0.06	-0.24	1260(sh)	1091	
<i>cis</i> -IIc	Me <sub>2</sub> Si	OMe	7.5—6.7(m)	6.44	3.43	3.38	0.23	0.18	1253	1090	
<i>trans</i> -IIc	Me <sub>2</sub> Si	OMe	7.6—6.8(m)	6.33	3.37	3.27	0.13	-0.19	1252	1089	
<i>cis</i> - $\alpha$ -IIc	MeSi	OMe	—	6.64	3.45	3.45	0.25	0.25	—	—	
<i>cis</i> - $\beta$ -IIc	(OMe) <sub>2</sub>	OMe	7.20(s)	6.24	3.30	3.48	0.15	0.25	1260	1081	
<i>trans</i> - $\alpha$ -IIc	Me <sub>2</sub> Si	OMe	—	6.43	3.45	3.28	0.08	-0.17	—	—	
<i>trans</i> - $\beta$ -IIc	Me <sub>2</sub> Si	OMe	7.4—6.8(m)	6.23	3.38	3.35	0.13	-0.42(?)	1258	1086	
<i>cis</i> -IIe	MeSi	OMe	7.24(s)	6.48	3.53	3.46	0.25	0.20	1260	1080	
<i>trans</i> -IIe	MeSi	OMe	7.6—7.8(m)	6.34	3.45	3.35	0.10	-0.38	1262	1084	
III	(OMe) <sub>2</sub>	OMe	7.23(s)	7.06	—	—	0.35	0.25	1250	930 <sup>c</sup>	
	Me <sub>2</sub> Si—O—SiMe <sub>2</sub>	—	—	—	—	—	—	—	—	—	

<sup>a</sup> Numbers of observed protons in each compound were in good agreement with those of the calculated. <sup>b</sup> See ref. 11. <sup>c</sup> Si—O—Si.

Scheme 1. A possible mechanism for the stereoselective and regioselective double silylation.



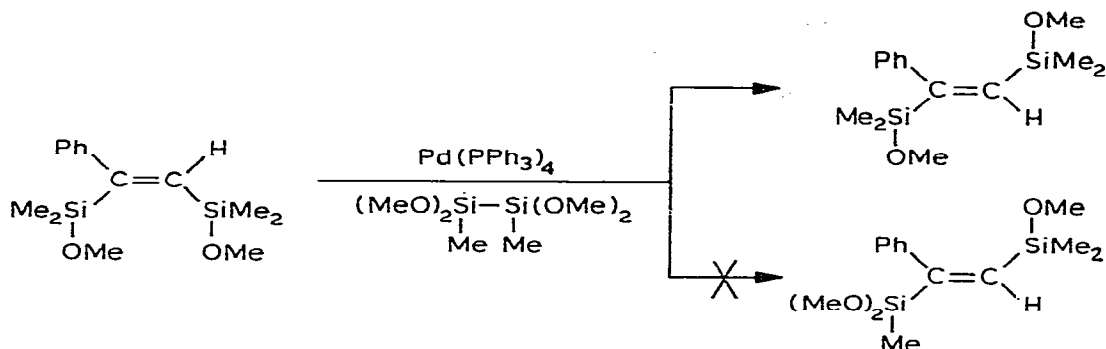
moiety possessing more methoxy groups to add to the  $\alpha$ -position also was observed in the reaction of phenylacetylene with II<sub>d</sub> which gave the predominant  $\alpha$ -adduct. Although the directive effects of methoxy groups cannot be fully understood at the present time, the reaction would proceed with the following geometry in a concerted transition state:



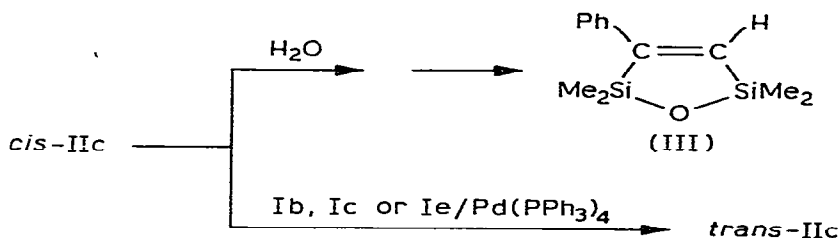
#### Isomerizations of *cis*-isomers catalysed by the Pd complexes with and without disilane

The *cis*-disilyl olefins were heated in the presence of the palladium(0) complex with or without disilane (Table 5). Thus, a mixture of the two isomers of II<sub>b</sub> (99% *cis* and 1% *trans*) was heated at 140°C in the presence of the catalyst and Ib. The *cis* and *trans* ratio decreased with time (60/40 and 54/46 after 4 and 24 h, respectively) (Run 2). In contrast, heating of an identical sample at 110°C without the disilane remained unchanged after 3 h (*cis/trans* 97/3) (Run 1).

Similarly, a 96/4 mixture of the *cis*-II<sub>c</sub> and *trans*-II<sub>c</sub> was kept at 110°C, 6 h in the presence of the catalyst and Ic afforded a *cis/trans* mixture of II<sub>c</sub> in a ratio of 70/30 (Run 4). It is of interest that, when Ib (Run 5) and Ie (Run 6) were employed in place of Ic, *cis*-II<sub>c</sub> similarly isomerized to *trans*-II<sub>c</sub>. However, in the both cases silicon exchanged products, as exemplified below, were not formed to any detectable extent. On the other hand, in the absence of any disilane (Run 3), no isomerization occurred, but there was obtained a siloxane,



III. This product was presumably formed via the hydrolysis of *cis*-IIc followed by the intramolecular cyclization. Kumada et al. had also observed a similar



cyclic siloxane from the reaction of acetylene dicarboxylate with *sym*-tetramethyldihydrodisilane [1].

The isomerization of *cis*-IIc occurred to only small extent, affording the *trans*-IIc with and without disilane. For example, a mixture of 90% *cis*- and 10% *trans*-isomer changed to 81% *cis*- and 19% *trans*-isomer (Run 9).

Surprisingly, the treatment of IIc using the complex  $\text{PdCl}_2(\text{PPh}_3)_2$  instead of  $\text{Pd}(\text{PPh}_3)_4$ , resulted in complete isomerization to the *trans*-isomer even after a short period of time (1 h, Run 7). This is in sharp contrast to the reaction of IIc with the palladium(0) complex which gave compound III. However, *cis*-IIe in the presence of  $\text{PdCl}_2(\text{PPh}_3)_2$  isomerized only slightly even after a long period of time. Thus, it appears that the ease with which the series of the isomerizations found in the present study depends not only on the nature of the catalyst systems but also on the structure of disilylolefins. The fact that the isomerization was effected more effectively by  $\text{PdCl}_2(\text{PPh}_3)_2$  than by the  $\text{Pd}(\text{PPh}_3)_4$  might suggest the electrophilic attack of the palladium species on the disilylolefins during isomerization.

## Experimental

All boiling points are uncorrected. The reactions were carried out by heating under an atmosphere of argon or in an evacuated Carius tube. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer, and  $^1\text{H}$  NMR spectra were measured on a Varian A-60D spectrometer in  $\text{CCl}_4$  solution with TMS as internal standard. GLC analyses were conducted using an Okhura Model 1700 gas chromatograph equipped with a 1 or 2 m  $\times$  4 mm Teflon column



TABLE 5  
ISOMERIZATION OF *cis*-ADDUCTS TO *trans* ISOMERS IN THE PRESENCE OF PALLADIUM COMPLEXES

Run	Substrates		Conditions			Product composition <i>cis/trans</i>
	Styrene <i>cis/trans</i>	Disilane	Catalyst <sup>a</sup>	Temperature (°C)	Time (h)	
1	<i>cis</i> - $\alpha$ -IIb 99/1	none	A	110	3	97/3
2	99 <sup>b</sup> /1	Ib	A	140	1	79/21
					4	60/40
					6	56/44
					24	54/46 <sup>c</sup>
3	<i>cis</i> - $\alpha$ -IIc 96/4	none	A	110	1	— <sup>d</sup>
					5	—
					22	—
4	96/4	Ic	A	110	2	93/7
					6	70/30
					21	35/65
5	92/8	Ib	A	110	1.5	82/18
					7	80/20
					24	75/25
6	92/8	Ic	A	110	3	77/23
					18	72/28
7	96/4	none	B	110	1	0/100
8	<i>cis</i> - $\alpha$ -IIId 90/10	none	A	140	1	86/14
					5	83/17
					25	78/22
9	90 <sup>e</sup> /10	Id	A	140	1	85/15
					4	83/17
					25	81/19 <sup>f</sup>
10	<i>cis</i> - $\alpha$ -IIe 95/5	none	A	110	2	95/5
					7	89/11
					24	89/11
11	95/5	Ie	A	110	2	94/6
					7	93/7
					24	91/9
12	98/2	Ib	A	110	22	93/7
13	83/17	Ic	A	110	1	83/17
					7	69/31
					23	61/39
14	94/6	none	B	110	3	92/8
					6	91/9
					23	87/13

<sup>a</sup> A: Pd(PPh<sub>3</sub>)<sub>4</sub>; B: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. <sup>b</sup> *cis*- $\alpha$ -IIb/*cis*- $\beta$ -IIb 81/19. <sup>c</sup> *trans*- $\alpha$ -IIb/*trans*- $\beta$ -IIb 79/21. <sup>d</sup> Main product: III; no isomerization occurred essentially. <sup>e</sup> *cis*- $\alpha$ -IIId/*cis*- $\beta$ -IIId 88/12. <sup>f</sup> *trans*- $\alpha$ -IIId/*trans*- $\beta$ -IIId 84/16.

packed with Silicone SF-96 (15–24%) on Celite 545-AW (column temp. 160–190°C; He carrier; an external standard, n-C<sub>14</sub>H<sub>30</sub>).

### Materials

All the methoxymethyldisilanes used were prepared via methoxylation of the corresponding chlorodisilanes according to the method reported previously

[4]. Mono-, di- and tri-chloromethylidisilane were obtained by chlorination [14] of hexamethylidisilane which was prepared by the literature method [15]. Dichlorotetramethylidisilane was also prepared via disproportionation of disilane fraction of the residue in the "Direct Synthesis" [16]. Phenylacetylene was commercially available and used after distillation. The two palladium [17, 18], the platinum [19], the two rhodium [20,21] and the nickel [22] triphenylphosphine complexes were prepared as described in the literature. Other materials were commercially available.

*Double silylation reaction of phenylacetylene in the presence of complex catalysts to form the cis-disilylated styrene derivatives*

*A. With symmetrical hexamethyl- and methoxymethyl-disilanes.* The method used for the addition reaction to give *cis*- $\alpha,\beta$ -bis(dimethylmethoxysilyl)styrene is representative. Under argon, a mixture of 1.8 g (10 mmol) of *sym*-dimethoxytetramethylidisilane (Ic), 0.51 g (5 mmol) of phenylacetylene and 58 mg ( $5 \times 10^{-2}$  mmol; 1 mol% relative to the acetylene used) of tetrakis(triphenylphosphine)palladium, Pd(PPh<sub>3</sub>)<sub>4</sub>, was heated at 110°C (oil bath) with magnetic stirring for 1.5 h. After cooling, the resulting mixture was subjected to GLC analysis. Two products which were isolated by preparative GLC were formed. From the elemental analysis and IR and NMR spectra, the minor product which had a shorter retention time than the major one was identified as *trans*- $\alpha,\beta$ -bis(methoxydimethylsilyl)styrene; the major product was as *cis*- $\alpha,\beta$ -bis(methoxydimethylsilyl)styrene. The total yield of the two products was 78% (by GLC based on the acetylene used) in which the composition of the *cis/trans* isomer was shown to be 92/8 (see Table 1). Pertinent physical, spectral and analytical data for all the compounds thus prepared are given in Tables 3 and 4.

Similarly, the reaction was carried out by means of an evacuated Carius tube in which the starting materials and the catalyst were mixed and sealed. The yield of the product thus formed after 20 h was 76% in a 91/9 mixture of the *cis/trans* isomer.

*B. With unsymmetrical methoxymethylidisilanes.* A typical method is given for the addition of methoxypentamethylidisilane (Ib) to yield the adduct IIb. The reaction was carried out using 3.2 g (20 mmol) of Ib, 1.0 g (10 mmol) of phenylacetylene and 116 mg (1 mol%) of Pd(PPh<sub>3</sub>)<sub>4</sub> at 110°C for 24 h in an evacuated Carius tube. The GLC analysis for the product mixture showed that the product was 65% in total yield and the isomer ratio of *cis* to *trans* was 99/1. From the reaction mixture a small amount of the *cis* isomer was isolated by preparative GLC and it was found by means of NMR analysis that this sample consisted of 81% *cis*- $\alpha$ -dimethylmethoxysilyl- $\beta$ -trimethylsilylstyrene (*cis*- $\alpha$ -IIb) and 19% *cis*- $\alpha$ -trimethylsilyl- $\beta$ -dimethylmethoxysilylstyrene (*cis*- $\beta$ -IIb). From the major part of the reaction mixture, a mixture of the *cis*- and *trans*-IIb boiling at 133°C/10 mmHg was isolated in 36% yield.

Likewise, from the same reaction under argon in an open system, the products were formed in the same isomer ratio and also in the same regioisomer ratio as the above (see Table 2).

### Isomerization of *cis*-II catalyzed by the Pd complexes with and without disilanes

Some typical examples for the isomerizations are shown below.

**A. Isomerization of *cis*-IIb.** A mixture of *cis*-IIb (2 mmol) (99% *cis* and 1% *trans*, the regioisomer ratio in the *cis* isomer being 81/19 for *cis*- $\alpha$ -IIb/*cis*- $\beta$ -IIb, respectively), methoxypentamethyldisilane (Ib) (2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg) was heated with stirring at 140°C for 24 h, during which time the reaction was monitored intermittently by GLC analysis of the mixture. The analyses showed that the peak corresponding to *cis*-IIb gradually decreased, while the peak due to *trans*-IIb appeared at a shorter retention time than that due to the *cis*-IIb. The intensity increased with the increasing reaction time. After 24 h, on cooling, the *cis/trans* isomer ratio was shown to be 54/46. The sample corresponding to the *trans* peak was isolated by preparative GLC and identified in the usual manner to be *trans*- $\alpha$ -dimethylmethoxysilyl- $\beta$ -trimethylsilylstyrene (*trans*- $\alpha$ -IIb) and *trans*- $\alpha$ -trimethylsilyl- $\beta$ -dimethylmethoxysilylstyrene (*trans*- $\beta$ -IIb) in 79 and 21%, respectively (Table 5, Run 2).

**B. Isomerization of *cis*-IIc.** A mixture of  $\alpha,\beta$ -bis(dimethylmethoxysilyl)styrene (IIc, 96% *cis* and 4% *trans*), *sym*-dimethoxytetramethyldisilane (Ic) (2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg) was treated under argon (110°C). On cooling after 6 h, the *cis/trans* ratio of the resulting mixture was 70/30 (Table 5, Run 4).

**C. Isomerization of *cis*-IIc with Ib.** A mixture of *cis*- $\alpha,\beta$ -bis(dimethylmethoxysilyl)styrene (IIc, 92% *cis* and 8% *trans*) (2 mmol), methoxypentamethyldisilane (Ib) (2 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg) was similarly treated (140°C; 24 h). The *cis/trans* ratio of the resulting mixture was 75/25 and no silicon exchanged components which are related to the isomerization, other than the *trans* compound, could be detected in the reaction mixture.

**D. Isomerization of *cis*-IIc in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> complex catalyst.** A similar treatment of a mixture of 96% *cis* and 4% *trans* of IIb (1.8 mmol) with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mg) (110°C; 1 h) gave only *trans* isomer. The product, isolated by preparative GLC, was shown by NMR analysis to be 100% *trans*-IIc.

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